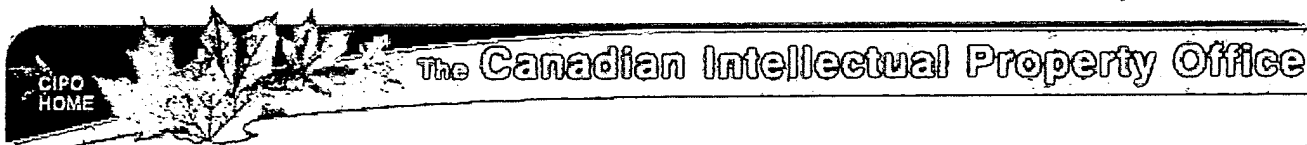


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(54) AQUEOUS COATING COMPOUND FOR ELECTRO DIP LACQUERING AND ITS  
USE FOR THE PREPARATION OF MULTILAYERED LACQUER COATS

(54) COMPOSE DE REVETEMENT AQUEUX POUR LAQUAGE ELECTROLYTIQUE  
ET SON EMPLOI DANS LA PREPARATION DE REVETEMENTS DE LAQUES  
MULTICOUCHES

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#### ABSTRACT:

ABSTRACT 1. Aqueous coating compound for electro dip lacquering. 2.1 Previous coating compounds containing polymer micro particles for electro dip lacquering had insufficient adherence to the substrate or to subsequently applied layers. A coating compound resulting in improved appearance combined with a smooth surface, good impact strength, good covering of the edges and improved rheological properties is to be provided. 2.2 In addition to containing film-forming resins and optionally cross-linking agents, pigments, solvents and conventional additives, the aqueous coating compound contains polymer powders having an average particle diameter of from 0.1 to 100 µm and a glass transition temperature of ?70°C, obtained from one or more

cross-linked urea-aldehyde resins, triazinealdehyde resins and phenol-aldehyde resins or one or more uncross-linked homo- or copolymers of acrylonitrile and/or methacrylonitrile and having a weight average molecular weight above 100,000 and containing at least 70% by weight of copolymerised acrylonitrile and/or methacrylonitrile or mixtures thereof, these powders being added to the coating compound after having been ground up with a triturating resin. 2.3 Preparation of; single layered or multi-layered lacquerings.

CLAIMS: [Show all claims](#)

\*\*\* Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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## ABSTRACT

1. Aqueous coating compound for electro dip lacquering.
- 2.1 Previous coating compounds containing polymer micro particles for electro dip lacquering had insufficient adherence to the substrate or to subsequently applied layers. A coating compound resulting in improved appearance combined with a smooth surface, good impact strength, good covering of the edges and improved rheological properties is to be provided.
- 2.2 In addition to containing film-forming resins and optionally cross-linking agents, pigments, solvents and conventional additives, the aqueous coating compound contains polymer powders having an average particle diameter of from 0.1 to 100  $\mu\text{m}$  and a glass transition temperature of  $\geq 70^\circ\text{C}$ , obtained from one or more cross-linked urea-aldehyde resins, triazine-aldehyde resins and phenol-aldehyde resins or one or more uncross-linked homo- or copolymers of acrylonitrile and/or methacrylonitrile and having a weight average molecular weight above 100,000 and containing at least 70% by weight of copolymerised acrylonitrile and/or methacrylonitrile or mixtures thereof, these powders being added to the coating compound after having been ground up with a tritulating resin.
- 2.3 Preparation of: single layered or multi-layered lacquerings.

## PATENT CLAIMS

1. Aqueous coating compound for electro dip lacquering, containing a binder of one or more water-soluble or water-dispersible film-forming resins and optionally one or  
5 more conventional cross-linking agents for the film-forming resins; as well as dispersed polymer particles and optionally pigments, solvents and/or conventional additives for lacquers, characterised in that it contains, as dispersed polymer particles, from 5 to 75% by weight, based  
10 on the solids content of the film forming resin and any cross-linking agent present, of polymer powders having an average particle diameter of from 0.1 to 100  $\mu\text{m}$  and a glass transition temperature of  $\geq 70^\circ\text{C}$ , and the polymer powders consist of
- 15 a) one or more cross-linked urea-aldehydes resins, triazine aldehyde resins and phenol aldehyde resins or  
b) one or more uncross-linked homo- or copolymers of acrylonitrile and/or methacrylonitrile having a weight average molecular weight ( $\bar{M}_w$ ) above 100,000 and contain-  
20 ing at least 70% by weight of copolymerised acrylonitrile and/or methacrylonitrile, or  
c) mixtures of a) and b),  
which have been added to the coating compound as a substance ground up with the binder, the water-dispersible film-  
25 forming resin or cross-linking agent and/or with a triturating resin, the coating compound and the triturating resin being free from components which dissolve or swell the polymer powder at temperatures of up to  $80^\circ\text{C}$ .
2. Aqueous coating compound according to Claim 1,  
30 characterised in that the polymer powders are substantially free from ionic or ionizable groups.
3. A process for the preparation of a multi-layered build-up on an electrically conductive substrate,

- 1 characterised in that an aqueous coating compound according to Claim 1 or  
Claim 2 is deposited electrophoretically as a priming coat whereupon  
another layer of lacquer or filler is applied.
- 5 4. Use of the aqueous coating compound according to Claim 1 or Claim 2 as  
cathodically depositable electro dip lacquering.
5. Use according to Claim 4 for the formation of priming coats for multi-  
layered lacquers.
- 10 6. A process according to Claim 3, characterised in that the priming coat  
is stoved before application of further layer of lacquer or filler.
7. A process according to Claims 3 or 4 for producing a stone chip  
15 resistant multi-layered build-up.

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Aqueous coating compound for electro dip lacquering and its use for the preparation of multilayered lacquer coats

This invention relates to an aqueous coating compound for electro dip lacquering containing a binder of one or more water-soluble or water-dispersible film forming resins and optionally one or more conventional cross-  
5 linking agents for film forming resins as well as dispersed polymer particles and optionally pigments, solvents and/or conventional additives for lacquers.

Electro dip lacquering is a known process for coating the surface of electrically conductive objects consisting, for example, of metal or plastics which are conductive  
10 or have been rendered conductive. In this process, the article which is to be coated is dipped in an aqueous coating bath and, in the case of cathodic deposition, the article is connected as cathode to a source of direct  
15 current and the coating compound is deposited on the surface of the workpiece by the current. The material adhering to the workpiece is then physically treated by air drying or heating to enable it to flow and may also be chemically cross-linked for producing a homogeneous,  
20 smooth surface which is resistant to stone chipping.

The coating compounds used for electro dip lacquering consist substantially of one or more electrically depositable resins which can be neutralised and thereafter dispersed in water and optionally other, not solely water-dispersible binders (plasticizers) or cross-linking agents,  
25 special trituration resins, pigments and fillers and any additives and auxiliary substances required. The properties of the films such as corrosion protection, levelling, resistance to stone chipping and adherence  
30 can be influenced by varying the composition of the resin components.

The coating of composite steel sheets with a suspension of a water-dispersible sol of a metal compound with an organic synthetic resin powder is described in DE-B-26 50 611. The coating deposited from this suspension is cured by heating, during which the synthetic resin powder melts at least temporarily. A water-soluble or water-dispersible polymer is added to the suspension to improve adherence.

Electro dip lacquer coating materials consisting of cationic synthetic resins which are to be protonated with acid and rendered soluble and of ionic synthetic resin powders dispersed therein are described in EP-A-0 052 831. These synthetic resin powders may contain pigments and fillers. These coating compounds also melt when stoved and undergo cross-linking to form a smooth coating. Ionic group-containing epoxide resins, polyester resins, acrylate resins, polyurethane resins and polyamide resins are described as synthetic resin powders which can be dispersed in the coating materials.

The coating compounds described in the literature mentioned above have the disadvantage that in the process of cross-linking, the film must be heated to a temperature above the melting temperature of the synthetic resin powder in order that a smooth coating may be obtained.

In EP-A-0 259 181 there are described coating compounds for electro dip lacquering based on electrically depositable water-dispersible resins in which the polymer particles have a softening point at least 10 degrees Centigrade higher than the bath temperature, a solubility parameter differing by not more than 1.0 from the solubility parameter of the water-dispersible resin, and a refractive index differing by from 0.02 to 0.3 from that of the water-dispersible resin or a cross-linking density of from 0.01 to 5.05 mmol/g. The surfaces of these polymer micro-particles contain ionic groups having the same polarity as the water-dispersible resin. The addition of the polymer microparticles is said to improve the wrap-around and



dispersion stability and impart to the coating a matt finish as well as controlling the fluidity in the process of electro deposition. Various disadvantages, however, are found in the known electro dip lacquered coatings, such as poor covering of the edges, poor adherence to the substrate or to subsequent coats and insufficient impact strength.

It is therefore an object of the present invention to provide aqueous coating compounds for electro dip lacquering which provide good adherence to the substrate or to subsequent coats, give rise to coatings with a smooth surface and high impact strength (for example, good protection against stone chipping), and manifest improved rheological properties during the stoving process and thus ensure good covering of the edges.

It has been found that this problem may be solved by means of an aqueous coating compound depositable at the cathode or anode in accordance with the generic concept defined above, characterised in that it contains, as dispersed polymer particles, from 5 to 75% by weight of polymer powders, based on the solids content of film-forming resin and any cross-linking agent present, which polymer powders are preferably free from ionic or ionisable groups, have an average particle diameter of 0.1 to 100  $\mu\text{m}$  and a glass transition temperature of  $\geq 70^\circ\text{C}$  (determined according to DSC = Differential Scanning Calorimetry), and the polymer powders consist of

- a) one or more cross-linked urea-aldehyde resins, triazine-aldehyde resins and phenol-aldehyde resins or
  - b) one or more uncross-linked homo- or copolymers of acrylonitrile and/or methacrylonitrile having a weight average molecular weight ( $\bar{M}_w$ ) of over 100,000 and containing at least 70% by weight of copolymerised acrylonitrile or
  - c) mixtures of a) and b)
- which up to a temperature of  $80^\circ\text{C}$  cannot be made to dissolve or swell by the binder, water-dispersible film-forming

resin, cross-linking agent, trituration resin or solvent present in the coating compound.

5 The polymer powders are added to the coating compounds as products which have been milled with the binder, the water-dispersible film-forming resin or cross-linking agent, in particular with a part thereof, and/or with a trituration resin.

10 It has been found in the context of the present invention that the coatings obtained by addition of the polymer powders to the aqueous coating compounds have a smooth surface and are free from surface defects such as pitting. For avoiding pitting, it is conventional to add additives or pigments which interfere with the levelling of the film in the stoving process and result in a markedly rough surface. Another disadvantage is that the adherence of subsequent coats is frequently impaired. These disadvantages are overcome by the present invention. In addition, it has been shown in the context of the present invention that the addition according to the invention of polymer powders gives rise to excellent rheological properties, this improvement being obtained in particular by the addition of urea-aldehyde resin powders, triazine-aldehyde resin powders and phenol-aldehyde resin powders. A uniformly matt surface is thus obtained and at the same time good covering of the edges. The properties may therefore be graded by adjusting the quantity of aldehyde-resin powder used. Further, exceptionally good adherence to the substrate or to subsequent coats is obtained in particular by the addition of polyacrylonitrile powders (homo- or copolymers). The impact strength is also improved, in particular also at low temperatures. The coating compounds according to the invention are therefore particularly suitable for the formation of layers protecting against stone chipping, for example in the construction of motor vehicles. These properties are still obtained when subsequent layers are applied. Optimum results in these properties can be obtained by adjusting the quantity of polyacrylo-

nitrile powder used.

The polymer micro particles used should not be dissolved or caused to swell by the binder, the trituration resin or any solvents in the binder at temperatures of up to 80°C. In other words, the micro particles should remain unchanged under the conditions of preparation and use.

The glass transition temperature is  $\geq 70^{\circ}\text{C}$  (determined according to DSC) and is chosen so that no softening of the cross-linked or uncross-linked polymer powders will occur under the conditions of preparation or application of the coating compounds since otherwise problems may arise when the polymer powders are milled (trituated) to form a paste, with the result that an unstable, inhomogeneous product is liable to be obtained. Observing this condition will also prevent swelling of the polymer powders.

Since treatment of the primer coat, such as rubbing down cannot always be avoided in the preparation of coatings, the stoved films must have suitable properties to allow for this; for example, they must be able to withstand treatment with sandpaper for a sufficient length of time. If the polymer powders soften at too low a temperature, the treatment agents rapidly become unusable.

A positive effect of the high glass transition temperature is also observed in the stoved film: Polymer powders having a glass transition temperature  $\geq 70^{\circ}\text{C}$  give rise to high impact strength.

The particle diameters of the polymer powders used should be sufficiently small within the given range of from 0.1 to 100  $\mu\text{m}$ , depending on the required thickness of the layer, to ensure that a homogeneous and smooth surface will be obtained on the deposited and stoved film. Although a rough, uneven surface in many cases ensures good adherence of the subsequent layers applied, it is unsuitable on account of the unsatisfactory optical effect obtained, e.g. in the case of primer coats for motor vehicles.

The aldehyde-resin powders used in the coating compounds according to the invention are highly cross-linked and have no melting point. The polyacrylonitrile powders used have a molecular weight ( $\bar{M}_w$ ) above 100,000. They are not chemically cross-linked but they have no melting point since they decompose at temperatures above 300°C before they can melt. The polymer powders used are chemically substantially inert, i.e. they do not react with the basic film-forming resins used.

The polymer powders used may be prepared by the conventional methods known to the man of the art and described in the literature. They may already be obtained as powders at the stage of preparation and these may then be ground down to the required particle size but with suitable control of the reaction conditions they may from the start be obtained in the required particle size. The powders obtained may be used after their separation from the reaction medium or they may be obtained in the form of aqueous suspensions. If suspensions are used, these need not be stable in storage and may undergo sedimentation. For their use in the coating compounds according to the invention, they are trituated (ground up) to form an aqueous paste which remains stable for some time. The usual tritulating binders may be used for this purpose and part of the binder or part of the film-forming resin or cross-linking agent may be used.

The particle size distribution of the polymer powders used may vary over a wide range. The composition of the powders may be used purposefully to influence special properties such as the rheological properties, provided only that the maximum particle diameter does not result in an inferior surface of the deposited, stoved lacquer film.

The polyacrylonitrile powders used may be prepared by conventional processes. Examples of suitable processes are the emulsion polymerisation or suspension polymerisation of acrylonitrile or methacrylonitrile, which are

well known to the man of the art and are described in "Chemische Technologie" by Winacker-Küchler, Volume 6, Organische Technologie 2, Karl Hans-Verlag Munich-Vienna 1982. The polyacrylonitrile polymer powders used according to the invention contain at least 70% of acrylonitrile and/or methacrylonitrile. One or more copolymerisable monomers may be added to the acrylonitrile and/or methacrylonitrile for preparing the copolymers. Examples of such monomers include acrylic esters and methacrylic esters of  $C_2$  to  $C_{22}$  alcohols, e.g. methyl methacrylate, butyl methacrylate, octyl methacrylate, ethyl acrylate, isobutyl acrylate, (meth)acrylic acid esters of perfluorinated  $C_1$  to  $C_{22}$  alcohols, aromatic vinyl compounds having up to 20 carbon atoms, e.g. styrene or vinyl toluene, the esters of maleic acid or fumaric acid with  $C_1$  to  $C_{22}$  alcohols, vinyl chloride, ethylene and butadiene.

Further examples of suitable comonomers include unsaturated carboxylic, sulphonic and phosphonic acids and esters thereof, such as crotonic acid, itaconic acid, vinyl sulphonic acid, acrylamidopropyl methane sulphonic acid, vinyl phosphonic acid and esters of these acids. Unsaturated primary, secondary and/or tertiary amines may also be used as comonomers, e.g. dimethylamino neopentyl methacrylate, dimethylamino neopentyl acrylate, 2-N-morpholino ethyl methacrylate, 2-N-morpholino ethyl acrylate and amides of acrylic or methacrylic acid, e.g. acrylamide, dimethylmethacrylamide or methyl butyl acrylamide.

Other functional monomers capable of copolymerisation may be used in addition. They may contain hydroxyl, silane or epoxide groups, e.g. vinyl trimethoxysilane, vinyl tributoxysilane, methacryloxypropyl trimethoxysilane, vinyl tris(methoxyethoxy)silane, vinyl triacetoxysilane, hydroxyethyl methacrylate, hydroxybutylacrylate, glycidyl acrylate, glycidyl methacrylate and polyhydroxy ethylacrylate.

The polyacrylonitrile powders used according to the invention should contain at least 70% by weight (based on

the quantity of monomers used) of acrylonitrile and/or methacrylonitrile and preferably contain above 90%. Properties of the polyacrylonitrile powders, e.g. their glass transition temperature, may be influenced by suitable choice of the monomers. The melt properties may also be influenced by these means. The particle size distribution can be influenced by suitable choice of the process of preparation and of the process parameters employed therein.

10 The preparation in aqueous suspension is generally carried out in the presence of suitable non-ionic, anionic or cationic emulsifiers. Conventional protective colloids may also be used, e.g. cellulose ethers, polyvinyl alcohols or polyvinyl pyrrolidones. Radical polymerisation is  
15 started with the aid of compounds conventionally used for initiating the formation of radical chains, e.g. azo compounds, peroxides, peresters or percarbonates. Examples of conventional initiator systems include azo-isobutyronitrile, benzoyl peroxide, dicyclohexyl peroxydicarbonate, hydrogen peroxide, sodium persulphate and  
20 tert.-butylhydroperoxide.

The choice of monomers, comonomers and conventional auxiliary agents is determined by the requirements to be met by the polyacrylonitrile powder, such as the particle  
25 diameter, the glass transition temperature, the molecular weight and the solution properties. After the polyacrylonitrile polymers have been prepared, they may be worked up in aqueous suspension (e.g. dispersed with a resin paste) or they may be dried to form powders and then  
30 used for the purpose according to the invention, optionally after a further milling process.

The cross-linked aldehyde polymer powders may be prepared by the reaction of urea, triazine and/or phenol with an aldehyde, preferably with formaldehyde or compounds  
35 which split off formaldehyde. The conditions concerning the quantities of reactants used, the reaction temperature and the reaction medium in which the reaction is carried

out may be chosen to produce cross-linked, infusible masses. The conditions required are well known to the man of the art.

5 Cross-linked triazine resins, among which the polymer masses of melamine aldehyde, benzoguanamine aldehyde and acetoguanamine aldehyde are preferred, cross-linked urea resins and cross-linked phenol resins are described, for example, in Methoden der Organischen Chemie (Houben-Weyl), Volume 2, Makromolekulare Stoffe, in the Chapters  
10 entitled "Polyadditions- bzw. Polycondensationsprodukte von Carbonyl- und Thiocarbonylverbindungen" on pages 193 to 365.

Cross-linked phenol aldehyde resins are also described, for example, in "Chemie der Phenolharze" by K.Hultzsch,  
15 Springer-Verlag, 1950, under the heading "Resit".

Infusible polymer masses obtained may be reduced to the required particle size, preferably by grinding processes using the known grinding devices for the size reduction of particles.

20 The synthetic resin powders used are substantially free from ionic groups on their surface, i.e. ionic groups are not required for further processing to produce electro-dip lacquer coating compounds, although the powders may contain ionic groups or acid or basic groups for  
25 the purpose of obtaining certain properties such as improved stability to dispersion. Synthetic resin powders containing acid groups may be used in the same manner as non-ionic powders for anodically and cathodically depositable electro dip lacquer coating compounds and  
30 synthetic resin powders containing basic groups may also be used for anodically and cathodically depositable electro dip lacquer coating compounds.

The binders used for the systems capable of being deposited at the anode or the cathode are conventional  
35 electro dip lacquer (ETL) binders or binder mixtures. They can be deposited at the cathode if they carry positively charged ionic substituents or substituents

capable of being converted into such ionic groups. They can be deposited at the anode if they carry negatively charged substituents or substituents capable of being converted into negatively charged groups.

5       The binders for anodically depositable dip lacquers (ATL) contain basic resins which may have acid numbers of from 35 to 300 and number average molecular weights of from 300 to 10,000 g/mol. The acid groups may be  $-\text{PO}_3\text{H}$ ,  $-\text{SO}_3\text{H}$  and/or, preferably,  $-\text{COOH}$ . Basic compounds are  
10       used as neutralizing agents, e.g. primary, secondary or tertiary amines containing aliphatic and/or aromatic groups, or ammonia.

      Examples of basic resins include the reaction products of maleic acid anhydride with

15       fatty oils or with synthetic oils such as polybutadiene oil, polyester resins, epoxy resin esters, polyurethane resins or poly(meth)acrylate resins. The basic resins may be self-cross-linking or cross-linked by other compounds. The cross-linking agents used may be triazine resins,  
20       phenol resins and/or blocked isocyanates. Binders of this type are widely described in the literature, e.g. in DE-A-28 24 418.

      The binders and cross-linking agents conventionally used for electro dip lacquering may be used for the preparation of the cathodically depositable dip lacquers (KTL)  
25       according to the invention. Examples include self-cross-linking, film-forming basic resins as well as basic film-forming resins which require an additional, conventional cross-linking agent, and mixtures thereof. The resins  
30       contain ionic groups or groups which are ionic after neutralization.

      Examples of the basic resins used in the coating baths are described in EP-A-0 082 291, EP-A-0 234 395 and EP-A 0 209 854. These resins are conventional amino  
35       epoxide resins containing primary, secondary or tertiary amino groups and having an amine number of from 45 to 120 and a hydroxyl number of from 50 to 500. The amine



number influences the solubility of the resin as well as the quality of the surface of the stoved lacquer film. The reactive hydroxyl groups and in some cases also the reactive amino groups are essential for the cross-linking reaction. Their number is at least 2, preferably not less than 4 per molecule. If the degree of cross-linking is too low, the films remain sensitive to external influences after they have been cross-linked. The epoxide resins may also be aliphatic or cycloaliphatic hydrocarbons which contain epoxide groups and may be prepared by epoxidation with peracids. The amino groups are advantageously introduced with the epoxide groups of the resin by the addition of the NH-reactive compounds. The use of an excess should be avoided in order to prevent contamination with low molecular weight NH products and side reactions.

Examples of other suitable binders include the reaction products of bisphenols such as bisphenol A or bisphenol F with primary amines and formaldehyde. These may be reacted with a conventional semi-masked isocyanate obtained as reaction product of an aliphatic and/or aromatic di- or polyisocyanate and a primary amine. The amines used may be aliphatic amines and/or alkanolamines. The reaction product should contain an average of one secondary amino group per molecule. Any OH group present may optionally be reacted with an epoxide compound and/or with further isocyanate groups.

Suitable binders are described, for example, in EP-A-0 261 385. They are obtainable by copolymerisation of glycidyl (meth)acrylates or allyl glycidyl ethers with unsaturated monomers. Examples of suitable unsaturated olefinic monomers include saturated linear or branched acrylic or methacrylic acid esters, styrene and functionalized acrylic acid and/or methacrylic acid esters. The amino groups necessary for imparting solubility may be introduced by reaction of the epoxide group with secondary amines or amino alcohols. Alternatively, they may be introduced by the incorporation by polymerisation

of linear or cyclic secondary or tertiary nitrogen-containing (meth)acrylic compounds in the ester group.

The resins may be self-cross-linking or cross-linked by external cross-linking agents. Examples of suitable cross-linking compounds include triazine resins, blocked isocyanates, cross-linking agents capable of transesterification or transamidation, and cross-linking agents containing terminal double bonds. These cross-linking agents are well known and described in the literature.

Cross-linking agents based on triazines are described e.g. in EP-A-0 245 786.

Suitable isocyanate compounds are described e.g. in "Farbe und Lacke", 12, 1983, pages 928 et seq. These are conventional di- or polyisocyanates based on aliphatic and/or aromatic isocyanates or mixtures thereof which are reacted with known blocking agents such as alcohols, phenols, oximes, lactams, hydroxymethacrylates, alkanolamines, substituted secondary amines or aromatic alcohols. Cross-linking agents of the transesterification or transamidation type are described in DE-A-34 36 345. They react with binders of binder systems containing heteroatoms which carry active hydrogen atoms, such as OH, SH or NH groups. They may also effect cross-linking by reactions with carboxylic acid esters or amides.

The resins may be used as individual components (self-cross-linking) or as mixtures. For this purpose, they are used in a solvent-containing form and partially neutralised with the required quantity of a conventional acid such as formic acid, acetic acid, an alkyl phosphoric acid or lactic acid, and they may then be dispersed in water. Polybasic acids such as phosphoric acid or citric acid may be used for special purposes.

It is preferred to use basic resins or mixtures of basic resins consisting to an extent of at least 30% by weight of amino epoxide resins. Amino epoxide resins based on bisphenol A-amino epoxides are particularly

advantageous. These are then cross-linked with conventional masked isocyanates or trans-esterification hardeners or a mixture of the two.

For incorporation of the polymer powders used according to the invention in the coating compounds, the polymer powders are triturerated (ground) to a paste. The polymer powders may be ground up into a paste together with the binder, the water-dispersible film-forming resin, the cross-linking agent or parts thereof and/or a triturerating resin (paste resin), optionally with the addition of solvent. This process may be carried out by, for example, dispersion in a high speed stirrer apparatus. The paste obtained may then be ground up in a suitable apparatus either immediately thereafter or after an intermediate period of storage. Any binder, resin, cross-linking, pigment and/or bath constituents not yet introduced may be added at this stage and further grinding may then optionally be carried out. The desired composition of coating compound may then be obtained by neutralization with a suitable quantity of neutralizing agent and the addition of water.

According to another method of carrying out the process, the usual film forming resins may be converted into the aqueous phase with the formation of a solution or dispersion after neutralization. The polymer powders are then introduced into this dispersion as a paste.

If the polymer powders used according to the invention are not triturerated in the binder, the binder components or parts thereof to form a paste, then resin pastes or triturerating resins are used such as those conventionally used as triturerating binders for the preparation of pigment pastes. Triturerating binders of this type are described, for example, in EP-A-0 107 088, EP-A-0 183 025 and EP-A-0 270 877. These binders have a high wetting capacity for pigments and fillers. They are required to be readily compatible with the binder of the aqueous coating compound and should not alter the properties of the binder mixture.

They may cross-link with the binder by way of functional groups.

Further, they may consist, for example, of reaction products of modified polyepoxides, preferably based on aliphatic or aromatic diols such as polyalkylene glycol or bisphenol A or phenol novolaks, with primary and/or secondary amino groups of aliphatic mono- and/or diamines. These compounds may be further modified, e.g. to form compounds containing oxazolidine rings, or they may be reacted with isocyanate group-containing compounds by way of H-reactive groups such as OH or NH.

Further examples include products based on polyepoxide resins of aromatic or aliphatic diols optionally modified with functional groups such as ester groups or masked isocyanate groups which may be reacted with polyphenols. These compounds are further reacted with primary or secondary or tertiary amines, e.g. alkylamines, dialkylamines, alkanolamines or trialkylamines or compounds which are functionalized in the side chain.

The tritulating binders are rendered soluble by the introduction of acid or basic groups into the molecule and neutralization of these groups with neutralizing agents (acid or basic). The groups introduced may be, for example, amino groups which may either be neutralized with a conventional acid or converted into quaternary ammonium groups by a reaction. The solubility may be adjusted by the number of acid or basic groups introduced, e.g. the amino functionalities.

The number of OH groups also has an influence on the dispersibility in water.

These aqueous pastes may be prepared, for example, by adding the quantity of acid necessary for neutralization to a conventional pigment tritulating resin dissolved in organic solvents and then converting the resin into a highly fluid aqueous dispersion by means of completely salt-free water and other auxiliary substances, e.g. wetting agents or solvents, and subsequently incorporating

the pigments by means of an apparatus equipped with high speed stirrer mechanism. Part of the film-forming resin may also be used.

5 The aqueous coating compounds according to the invention contain the usual additives, pigments and solvents used for lacquers in addition to the polymer powders, the binders and, if used, cross-linking agents. Conventional pigments and fillers may be used, e.g. carbon black, titanium dioxide, finely dispersed silicon dioxide, 10 aluminium silicate, metal effect pigments, organic and inorganic colour pigments and pigments protecting against corrosion, such as lead and chromate compounds. The pigments and fillers may be worked up into pastes together with the polymer powders used according to the invention 15 or they may be made up into pigment pastes separately, using the same binders, binder constituents and paste resins as those used for tritulating the polymer powders used according to the invention.

The pastes thus prepared (pastes containing the polymer 20 powders used according to the invention, pigment pastes and/or pastes containing polymer powders and pigments) are adjusted to a suitable viscosity for grinding by the addition of completely salt-free water or solvents and are then ground in a conventional apparatus suitable for this purpose. Further 25 additives may be introduced after the process of dispersion. The pastes obtained are aqueous and have a low specific gravity. They have a high solids content and yet have a high resistance to sedimentation and viscosity changes in storage.

30 Electro dip lacquer coating baths may then be prepared from an aqueous dispersion of the binders and pigment pastes. These baths are diluted to the required solids content with water and may then be used as coating baths for metallic or conductive substrates as known to the 35 man of the art. When the deposited films have levelled out and cross-linked, dense, homogeneous electro dip lacquer coatings are obtained. These are distinguished

by their good surface, good covering of the edges, good resistance to stone chipping and low density. Due to the low density of the coating baths, the tendency to sedimentation is very slight and the yield is very high.

5        Levelling out and cross-linking may take place at room temperature or at an elevated stoving temperature. Further, one or more than one additional layer may be applied to the lacquer coat obtained. Cross-linking may be carried out after application of each individual lacquer  
10 coat or coating is carried out wet-in-wet and all the layers are then stoved together in a single stoving operation.

For example, a top coat lacquer or a filler and other layers may be applied before or after stoving of the layer which has been electrically deposited according  
15 to the invention from an aqueous solution or dispersion. The following build-up of lacquer is suitable for producing a metallic effect on car bodies: Cathodically deposited electro dip primer, filler (aqueous or non-aqueous),  
base lacquer (aqueous or non-aqueous) containing aluminium  
20 particles and pigments and/or dyes, and transparent top coat lacquer (aqueous, non-aqueous or from lacquer powder). An aqueous or non-aqueous intermediate undercoat for protecting against stone chipping may be applied to the primer layer before application of the filler.

25        Apart from being suitable for lacquering car bodies, the coating compounds according to the invention are suitable for use as industrial lacquers, for example for lacquering refrigerators, washing machines, office furniture, agricultural machinery, building machinery,  
30 screws, springs and accessories and fittings for motor vehicles.

In the following Examples, all percentages and parts (T) are based on weight. The solids content is determined at 150°C by a method analogous to that of DIN 53 182.

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Preparation of binders:Example 1

391 g of Diethanolamine, 189 g of 3-(N,N-dimethylamino)-propylamine and 1147 g of an adduct of 2 mol of hexane-1,6-diamine and 4 mol of the glycidyl ester of versatic acid (Cadura<sup>R</sup> E 10 of Shell) are added to 5273 g of bisphenol A epoxide resin (epoxide equivalent weight about 475) in 3000 g of ethoxypropanol as described in EP-A-12 463. The reaction mixture is maintained at 85 to 90°C for 4 hours with stirring and then at 120°C for one hour. Ethoxypropanol is then added to dilute the reaction mixture to a solids content of 60%.

Example 2

228 Parts of bisphenol A (1 mol) are reacted with 260 parts of diethylaminopropylamine (2 mol) and 66 parts of para-formaldehyde (91%, 2 mol) in the presence of 131 parts of toluene as azeotropic entraining agent until 42 parts of the water of reaction have been removed. After the addition of 152 parts of diethylene glycol dimethylether and cooling of the product to 30°C, 608 parts (2 mol) of a tolylene diisocyanate half blocked with 2-ethylhexanol are added in 45 minutes. When the isocyanate value has been virtually reduced to zero, 1400 parts of this solution are mixed with a solution of 190 parts of an epoxide resin based on bisphenol A (epoxide equivalent weight about 190) and 250 parts (1 mol) of a glycidyl ester of a saturated tertiary C<sub>9</sub> to C<sub>11</sub> monocarboxylic acid in 389 parts of diethylene glycol dimethylether and the mixture is reacted at 95°C to 100°C until the epoxide value is 0.

Example 3

a) 832 Parts of the monocarbonate of Epicote 828 are mixed with 830 parts of Capa 205 and 712 parts of diglycol dimethylether and reacted at 70 to 140°C with approximately 0.3% of BF<sub>3</sub>-etherate until the epoxide number is 0. 307 Parts of a reaction product of 174 parts of tolylene diisocyanate (2 NCO equivalents) and 137 parts of

2-ethylhexanol with the addition of 0.3% of benzyl trimethylammonium hydroxide (Triton B) having an isocyanate content of about 12.8% are added to this product (solids content 70%, two carbonate equivalents) at 40 to 80°C in the presence of 0.3% of Zn-acetylacetonate as catalyst. The reaction is carried out until the isocyanate value has been reduced to about zero and the reaction mixture is then adjusted to a solids content of about 70% with diglycoldimethylether.

b) 618 Parts of a reaction product obtained from 348 parts of tolylene diisocyanate (80% 2,4-isomer; 20% 2,6-isomer) and 274 parts of 2-ethylhexanol with the addition of 0.3% of benzyl trimethylammonium hydroxide as catalyst and having a residual NCO content of 12.8% are slowly added to 1759 parts of a bis-carbonate based on Epicote 1001<sup>R</sup> at 60 to 80°C together with 0.3% of Triton B<sup>R</sup> as catalyst. The reaction is continued until the NCO value has been reduced to approximately 0. The product obtained has a solids content of 70%. 622 Parts of the reaction product obtained from 137 parts of 2-ethylhexanol and 174 parts of tolylene diisocyanate with benzyl trimethylammonium hydroxide catalysis (0.3%) (NCO content about 12.8%) are added at 20 to 40°C to 860 parts of bis-hexamethylene triamine dissolved in 2315 parts of methoxypropanol and the components are reacted together until the NCO content is approximately 0. 4737 Parts of the reaction product b) and 3246 parts of reaction product a) (in each case 70% in diglycoldimethylether) are then added and the reaction is carried out at 60 to 90°C. The reaction is terminated at an amine number of about 32 mg KOH/g. The resulting product has a solids content of 60%.

#### Example 4

768 g of Trimellitic acid anhydride and 2000 g of a glycidyl ester of a branched tertiary C<sub>10</sub>-monocarboxylic acid (Cadura E10<sup>R</sup>) are carefully heated to 190°C with stirring, an exothermic reaction beginning at 90°C.



The reaction mixture is cooled to 140°C and 2.75 g of N,N-dimethylbenzylamine are added. The temperature is then maintained at 145°C until the acid number is below 3 mg KOH/g. A calculated quantity of Cadura R E10 is added if necessary. The reaction product is diluted to a solids content of 80% with 2-butoxyethanol.

#### Example 5

160 g of Caprolactam are slowly added with stirring to 431 g of a solution (75% in ethyl acetate) of a reaction product of 3 mol of tolylene diisocyanate and 1 mol of trimethylolpropane (Desmodur L<sup>R</sup>) at 70°C. The reaction mixture is then maintained at 70°C until the NCO content has virtually fallen to zero. 2-Butoxyethanol (204 g) is then added and the ethyl acetate is distilled off through a column until a solids content of 70% is obtained.

#### Example 6

647 g of a reaction product of 800 g of refined linseed oil and 200 g of maleic acid anhydride (mixing and heating to 200°C under inert gas until a sample gives no colour reaction with dimethylamine) are reacted with 162 g of colophony-maleic acid anhydride glyceric ester (Alresat KM 201<sup>R</sup>) for one hour at 160°C and neutralized with 82 g of trimethylamine at 100°C. The product obtained is dispersed in 1946 g of water.

#### Preparation of binder dispersions:

##### Example 7

A mixture is prepared from 300 g of a resin from Example 1 and 700 g of a resin from Example 2 (based on the solids content). This mixture is substantially freed from solvent by distillation. 45 g of lactic acid (50%) are then added and the mixture is converted into a dispersion with a solids content of about 43% by the addition of completely salt-free water in the heat.

##### Example 8

550 g of a resin from Example 1, 79 g of a resin from Example 4 and 1740 g of a resin from Example 3 are mixed together. The mixture obtained is substantially

freed from solvent by distillation under vacuum and 63.5 g of 20% formic acid are added with stirring. The reaction mixture is then converted into a dispersion with a solids content of about 38% by dilution with completely salt-free water.

Preparation of pigment pastes:

Example 9

180 g of Dibutyl tin oxide and 295 g of basic lead silicate are added with vigorous stirring to 110 g of 2-butoxyethanol, 10 g of 2,4,7,9-tetramethyl-5-decine-4,7-diol, 11 g of acetic acid, 310 g of a binder according to EP-A-0 183 025, Example 3 (55% in 2-butoxyethanol) and 340 g of completely salt-free water. The paste obtained is adjusted to a suitable viscosity with about 100 g of ethoxypropanol and ground to the required particle size in a pearl mill.

Example 10

9.5 g of Formic acid (50%), 518 g of a commercial cross-linked urea formaldehyde powder having a glass transition temperature of 85°C and particle sizes ranging from less than 1 to 22 µm are added to 233 g of a paste resin according to EP-A-0 138 025, Example 3, 55% in 2-butoxyethanol, using a high speed stirrer, and 1150 g of completely salt-free water are added and the mixture obtained is ground in a pearl mill. After grinding, 730 g of a paste according to Example 9 and 1150 g of completely salt-free water are added with further vigorous stirring. A stable pigment paste is obtained, whose solids content may be adjusted if necessary.

Example 11

The procedure is the same as in Example 10 but with only 345 g of urea formaldehyde powder and the addition of 173 g of a commercial polyacrylonitrile powder containing about 7% of methyl acrylate and having a glass transition temperature (according to DSC) above 90°C, a molecular weight above 100,000 and a particle size of from <1 to 95 µm. The paste obtained is ground down to the

required fineness of grain and adjusted to a suitable viscosity for storage by the addition of water.

Example 12

5 The procedure is the same as in Example 10 but with only 172 g of a urea formaldehyde powder and the addition of 72 g of a high molecular weight commercial polyacrylonitrile powder containing about 0.7% of methyl acrylate as comonomer and having a molecular weight of 400,000, a glass transition temperature (according to DSC) of  
10 75°C and a particle size range of from 3 to 12  $\mu\text{m}$ , and 174 g of titanium dioxide. A stable pigment paste is obtained.

Example 13

15 175 g of a paste resin according to EP-A-0 183 025, Example 3 (55% in butyl glycol) are mixed with 5 g of acetic acid (100%), 800 g of completely salt-free water, 300 g of a paste of Example 9, 400 g of a polyacrylonitrile powder analogous to that of Example 12 and 30 g of carbon black, using an apparatus with high speed  
20 stirrer, e.g. a dissolver. After adjustment of the viscosity with about 60 g of water, the mixture is ground to the required particle size in a pearl mill and the viscosity may subsequently be adjusted for storage if necessary.

Preparation and use of an anodically depositable lacquer:

25 Example 14

500 g of a resin from Example 6 are mixed with 48 g of a urea formaldehyde powder analogous to that of Example 10 and with 72 g of a polyacrylonitrile powder analogous to that of Example 11 and the mixture is ground in a  
30 pearl mill. The mixture is then diluted with 1100 g of the binder from Example 6 and made up into an anodically depositable lacquer by the addition of 1480 g of completely salt-free water. This lacquer is deposited under the usual conditions. A homogeneous, smooth and elastic film  
35 is obtained.

Preparation and use of cathodically depositable lacquers:Example 15

1100 g of a dispersion from Example 7 are diluted with 1540 g of completely salt-free water and 360 g of a paste from Example 10 are added with vigorous stirring. Steel sheets are coated at the cathode in known manner and stoved at 180°C for 30 minutes.

The surface of the film (20  $\mu$ m) is smooth, homogeneous and uniformly matt. The edges of the substrate are uniformly covered.

Example 16

1100 g of a dispersion from Example 7 are diluted with 1540 g of completely salt free water and 360 g of a paste from Example 11 are added with stirring. Steel sheets are coated at the cathode and stoved as in Example 15. A film having a thickness of about 20  $\mu$ m is obtained. The film is smooth with a tough elasticity and uniformly semi-matt.

Example 17

1250 g of a dispersion from Example 8 are diluted with 1200 g of completely salt-free water. 360 g of a paste from Example 12 are then added. The solids content is adjusted to about 19% by the addition of water. This cathodic dip lacquering (KTL) bath is used to coat steel sheets and the coatings are cross-linked as in Example 15. The dry film thickness is about 30  $\mu$ m. The surface is homogeneous, smooth, tough-elastic and semi-matt. The adherence to the substrate is satisfactory.

Example 18

550 g of the binder from Example 1, 31 g of the binder from Example 4 and 169 g of the binder from Example 5 are mixed with 3.7 g of formic acid (50%) per 100 g of solids content in a dissolver. 400 g of a paste from Example 13 are added and the mixture is then slowly diluted with 1900 g of completely salt-free water. After the mixture has been stirred for at least 24 hours, it is used for coating steel sheets and the coatings are stoved

at 165°C for 30 minutes. The surface is homogeneous, smooth and tough-elastic.

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